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WATER-BASED RUST-PROOFING COATING COMPOSITION
[SUISEI BOSA TORYO SOSEIBUTSU]

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1. Name of this invention

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WATER-BASED RUST-PROOFIGN COATING COMPOSITION

2. Claim(s)

[Claim 1] Water-based rust-proofing coating composition obtained by combining (A) an aqueous resin emulsion of an oxydatively polymerizable copolymer of 5,000 - 500,000 average molecular weight, comprising a monomer component consisting of (i) 2 - 60 wt% of a fatty acid-modified monomer resulting from reaction between drying oil fatty acid and/or semi-drying oil fatty acid and/or aziridiny α,β -ethylenically unsaturated carboxylic acid ester and (ii) 98 - 40 wt% of other ethylenically unsaturated monomers copolymerizable therewith, and (B) a rust-proofing pigment.

3. Detailed Explanation of this Invention

This invention pertains to a water-based rust-proofing coating composition and is particularly associated with a water-based rust-proofing coating composition containing an aqueous resin emulsion of an oxydative and polymerizable copolymer and a rust-proofing pigment as its essential components.

Generally speaking, a paint composition containing an aqueous emulsion type resin vehicle easily causes permeation of water content through the coated film, resulting in inferior water resistance and corrosion-resistance when coated over a metal, etc. Even if a rust-

* Numbers in the margin indicate pagination in the foreign text.

proofing pigment is added to this type of composition, the paint stability worsens, and improvement of corrosion-resistance cannot be obtained. On the other hand, a paint prepared by adding a rust-proofing pigment in a solvent type paint such as alkyd resin can provide improved pigment stability, water-resistance, and corrosion-resistance compared with the aqueous emulsion type paint. However, this solvent type paint has insufficient adhesiveness to a metal surface, low alkali resistance, flammability unique to the solvent paint, and difficult processibility.

Therefore, the industry needs a new type of an aqueous paint composition providing excellent adhesiveness to a metal surface, alkali resistance, water resistance, corrosion-resistance, and pigment stability. The developers of this invention conducted various researches on an aqueous emulsion of an oxydative and polymerizable copolymer having the constitutional monomer components consisting of a fatty acid-modified monomer resulting from reaction between drying oil fatty acid and/or semi-drying oil fatty acid and/or aziridinyl α,β -ethylenically unsaturated carboxylic acid ester and other ethylenically unsaturated monomers copolymerizable therewith. Thereby, they discovered that a paint composition comprising an aqueous solution or dispersion liquid consisting of an emulsion thereof and oxidative and polymerizable resin (for example) was processed into a three-dimensional structure by oxidative polymerization after coated, subsequently providing an extremely

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strong film (refer to Pat. No. 57-120151). Furthermore, after adding further investigations on various characteristics of the aqueous emulsion itself, the developers of this invention discovered that, once coated, the aqueous emulsion was processed into three-dimensional structure to form a coated film having not only excellent water resistance and corrosion-resistance, but also excellent pigment stability when a rust-proofing pigment was added to provide further improvement of the corrosion-resistance by the rust-proofing pigment. Furthermore, the paint was found to provide far stronger adhesiveness to a metallic surface and alkali resistance compared with the conventional alkyd resin solvent type rust-proofing paint. Thereby, the present invention was completed.

That is, this invention provides a water-based rust-proofing coating composition obtained by combining (A) an aqueous resin emulsion of an oxydative and polymerizable copolymer of 5,000 - 500,000 average molecular weight, comprising a monomer component consisting of (i) 2 - 60 wt% of a fatty acid-modified monomer resulting from reaction between drying oil fatty acid and/or semi-drying oil fatty acid and/or aziridinyl α,β -ethylenically unsaturated carboxylic acid ester and (ii) 98 - 40 wt% of other ethylenically unsaturated monomers copolymerizable therewith, and (B) a rust-proofing pigment.

The aqueous resin emulsion used as a color-developing agent in the rust-proofing coating composition can be easily prepared by the

following method as explained in the Patent No. 57-117255 and 57-117256 disclosed by the developers of this invention:

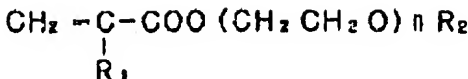
The materials (i) and (ii) described below are emulsification polymerized in an aqueous medium in the presence of a surfactant or high molecular protecting colloid,

or monomer (I) having an emulsion function described below or negative ion type monomer described below (II) is used as a part of copolymerizable ethylene type unsaturated monomer and emulsifying-polymerized in an aqueous medium in the absence of surfactant or high molecular protecting colloid:

(i) 2 - 60 wt% of a fatty acid-modified monomer resulting from reaction between drying oil fatty acid and/or semi-drying oil fatty acid (e.g., paulownia oil, dehydrated castor oil, linseed oil, safflower oil, soy oil, sesame oil, mustard oil, tall oil, Nuka oil, corn oil, sunflower oil, etc.) and/or of α,β -ethylenically unsaturated aziridinyl ester (e.g., aziridinyl acrylate);

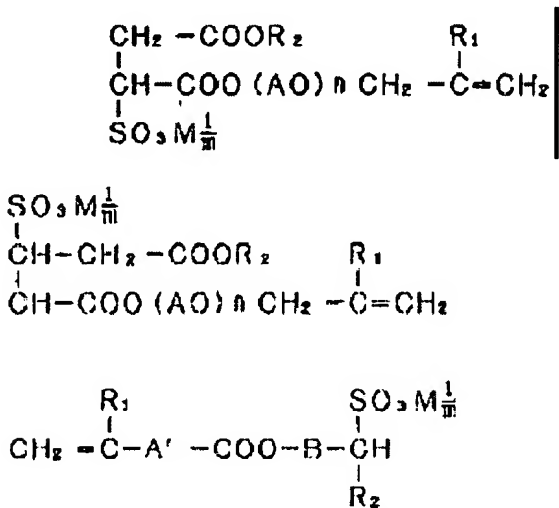
(ii) 98 - 40 wt% of other copolymerizable α,β -ethylenically unsaturated monomers (e.g., unsaturated amide compound, such as acrylic acid, methacrylic acid, and their hydroxyl alkyl ester, alkyl ester, acryl amide, and methacryl amide; styrene type monomer, such as styrene, vinyl toluene, α -methyl styrene, etc.; unsaturated nitril, such as acrylonitrile, methacrylonitrile, etc.; and acetic acid vinyl; etc.)

(I) Nonionic monomer expressed as:



(R₁ denotes a hydrogen, low class alkyl or halogen; R₂ denotes a hydrogen or low class alkyl; and n denotes a positive integer of 4 - 25.)

(II) Negative ion type monomer expressed as:



(R₁ denotes a hydrogen or methyl; R₂ denotes a saturated or unsaturated hydrocarbon or substituted hydrocarbon, or organic group containing an oxyalkylene group; A denotes an alkylene having 2 - 4 carbons or substituted alkylene group; M denotes a hydrogen alkali metal, alkali earth metal, ammonium, or organic amine; m denotes an atomic value of M or ion value; n denotes 0 or a positive integer; A' denotes a saturated or unsaturated hydrocarbon or substituted hydrocarbon group having 1 - 20 carbons; or hydrogen or low class alkyl; and B denotes a saturated hydrocarbon group having 1 - 6 carbons.)

Moreover, the rust-proofing pigment used in this invention may be any arbitrary known rust-proofing pigment as long as it does not react with water. Typical examples are lead type pigments, such as minium, zinc salt, lead sub-oxide, cyanamide lead, lead acid calcium, etc.; chromic acid salt pigments, such as zinc chromate, basic chromic acid lead, barium chromate, etc.; basic sulfuric acid lead, strontium chromate, black lead, phosphoric acid zinc, phosphoric acid calcium, zinc oxide, ferrite, phosphorous piece type iron oxide, phosphorous molybdenum acid aluminum, molybdenum acid zinc, phosphoric acid lead, molybdenum acid calcium, metha boric acid barium, metallic salt of organic nitro compound, syanamide lead calcium, silicate lead, molybdenum acid barium, phosphoric acid chrome; etc. However, the materials usable for this invention are not limited to those substances.

This invention is based on the discovery that a strong film can be formed by arbitrarily composing the abovementioned an aqueous resin emulsion and rust-proofing pigment not reacting with water, allowing the coated resin to be processed into three-dimensional structure by oxidative polymerization, providing further improved corrosion-resistance with the rust-proofing pigment. Therefore, the amounts of resin emulsion and rust-proofing pigment can be modifiable in a wide range depending on the desired effects, etc. However, normally, the amount of fatty acid modifiable oxidatively polymerizable aqueous emulsion resin should be 99 - 60 wt% (as a

solid substance), and the amount of rust-proofing pigment is preferably 1 - 40 wt%.

The balance of the paint composition of this invention is a water medium or a mixture of water medium and other additives added if necessary (e.g., pigment dispersant for forming a paint, defoaming agent, film forming helper, constitutional pigment, etc.) If necessary, an aqueous solution of oxidative polymerizing resin or water dispersion liquid can be added to the composition of this invention. To form a paint from the composition, any particular technique or device is needed, as the conventional method can be used.

The composition of this invention is used as a paint for providing corrosion-resistance and rust-proofing/protection for a metallic surface, particularly iron and zinc surfaces. As described above, the composition of this invention (1) has excellent pigment stability which is not achievable by composing a rust-proofing pigment in a regular emulsion paint, (2) provides excellent water resistance and corrosion-resistance far superior to the emulsion type paint, (3) offers the adhesiveness to a metallic surface and alkali resistance far better than the alkide solvent type paint containing a rust-proofing pigment, and (4) is free from the flammability and workability problem experienced with the solvent type paint. Therefore, the paint is an ideal rust-proofing paint for providing corrosion-resistance and protection to the metallic surface.

Hereafter, this invention is further explained by referring to operational and comparison examples. Parts in the examples denote weight parts.

Operational example 1:

(A)

Iron oxide (Toda Color KNO, by Toda Kogyo)	5 parts
Cyanamide lead (rust-proofing pigment)	15
Calcium carbonate (Super 3S, by Maruo Calcium)	15
Pigment dispersant (SMA1440H, by Daiichi Kogyo Yakuhin)	5
Water	10

(B)

Fatty acid modifiable oxidative polymerizing aqueous emulsion described in the reference example 1

(resin solid substance amount)	25 parts
Ethylene glycol	5
Water	19.5
Naphtene acid cobalt (Dicknate 3111, by Dainihon Ink Kagaku)	0.5

The material (A) was well stirred and pulverized into 50 μ or less granular diameter using a sand grinder mill. Then, the material (B) was added under stirring to prepare an aqueous paint composition (1).

Operational example 2:

(A)

Iron oxide (Toda Color KNO, by Toda Kogyo)	5 parts
Phosphoric acid zinc (rust-proofing pigment)	15
Calcium carbonate (Super 3S, by Maruo Calcium)	15
Pigment dispersant (SMA1440H, by Daiichi Kogyo Yakuhin)	5
Water	10

(B)

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Fatty acid modifiable oxidative polymerizing aqueous emulsion described in the reference example 2

(resin solid substance amount)	25 parts
Ethylene glycol	5
Water	19.5
Naphtene acid cobalt (Dicknate 3111, by Dainihon Ink Kagaku)	0.5

The material (A) was well stirred and pulverized into 50 μ or less granular diameter using a sand grinder mill. Then, the material (B) was added under stirring to prepare an aqueous paint composition (2).

Operational example 3:

(A)

Iron oxide (Toda Color KNO, by Toda Kogyo)	5 parts
Cyanamide (rust-proofing pigment)	15
Calcium carbonate (Super 3S, by Maruo Calcium)	15

Water-soluble styrene acrylic resin (as the
solid resin amount) 10

Water 10

Non-evaporative substance 50% Solvent

Water/butyl cellosolve = 4/1

Acid value 55% Neutralized

100% neutralized with ammonium water

Water 10

(B)

Fatty acid modifiable oxidative polymerizing aqueous emulsion
described in the reference example 1

(resin solid substance amount) 20 parts

Ethylene glycol 5

Water 19.5

Naphtene acid cobalt (Dicknate 3111, by Dainihon

Ink Kagaku) 0.5

The material (A) was well stirred and pulverized into 50 μ or
less granular diameter using a sand grinder mill. Then, the material
(B) was added under stirring to prepare an aqueous paint composition
(3).

Operational example 4:

(A)

Iron oxide (Toda Color KNO, by Toda Kogyo) 5 parts

Cyanamide (rust-proofing pigment) 15

Calcium carbonate (Super 3S, by Maruo Calcium)	15
Water-soluble styrene acrylic resin in the reference example 4 (as the solid resin amount)	10
Water	10

(B)

Fatty acid modifiable oxidative polymerizing aqueous emulsion
described in the reference example 3

(resin solid substance amount)	20 parts
Ethylene glycol	5
Water	19.5
Naphtene acid cobalt (Dicknate 3111, by Dainihon Ink Kagaku)	0.5

The material (A) was well stirred and pulverized into 50 μ or
less granular diameter using a sand grinder mill. Then, the material
(B) was added under stirring to prepare an aqueous paint composition
(4).

Reference example 1:

(A)

Safflower oil fatty acid	236 parts
Methacrylic acid glycidyl	131
Hydroquinone	0.4
Tetra ethyl ammonium bromide	0.2
Ethyl cellosolve	89

The abovementioned substances (A) were put in a reaction vessel and reacted under stirring at 130 - 140°C. The epoxy group and carboxy group addition reaction was traced while the remaining carboxyl group amount was measured. The reaction needed about 4 hours for completion. Then, the solvent was removed from this product at 120°C at a reduced pressure under stirring.

(B)

220 parts of deionized water, 1.0 part of edecyl benzene sulfonic acid sodium (Neopelex No. 6; Kao Sekken), and 2.7 parts of polyoxy ethylene sorbitene monolaurate (Tween 20; Kao Sekken) were /439 put in a 1-liter Erlenmeyer flask equipped with a stirrer, cooling device, temperature control device, and nitrogen guiding tube and heated to 50°C under stirring. Also, separately, 1.75 parts of ammonium persulfuric acid were dissolved in 80 parts of deionized water, and 1.75 parts of sulfurous acid were dissolved in 80 parts of deionized water. Moreover, 2.5 parts of the abovementioned surfactant (i.e., dodecyl benzene sulfonic acid sodium) and 10.6 parts of polyoxy ethylene sorbitene monolaurate were dissolved in 140 parts of deionized water, to which a mixture of 140 parts of 3-(a) additive reaction substance, 28 parts of styrene, 87.5 parts of methacrylic acid ethyl, 70 parts of methacrylic acid 2-ethyl hexyl, 21 parts of methacrylic acid hydroxyl ethyl, and 3.5 parts of acrylic acid was slowly added under stirring. Then, about 5 minutes later, the reacted monomer pre-emulsion was obtained. After confirming that

the emulsifier aqueous solution in the 1-liter Erlenmeyer flask was 50°C, the persulfuric acid ammonium aqueous solution and sulfurous acid hydrogen sodium aqueous solution prepared beforehand were dripped separately for 3 hours and 30 minutes for completely dripping the materials. After about 15 minutes, the pre-emulsion prepared beforehand was dripped for 3 hours under nitrogen gas flow. After the completion of dripping the aqueous solution as a reaction initiator, the temperature was maintained at 60°C to complete the reaction. With this method, an emulsion (non-evaporative substance = 40.4%, viscosity = 200 cp, and average molecular count = 120,000) was obtained.

Reference example 2:

(A)

Linseed oil fatty acid	237 parts
Methacrylic acid glycidyl	119
Hydroquinone	0.4
Tetra ethyl ammonium bromide	0.2

The abovementioned substances (A) were put in a reaction vessel and reacted under stirring at 170 - 180°C. The epoxy group and carboxy group addition reaction was traced while the remaining carboxyl group amount was measured. The reaction needed about 3 hours for completion.

370 parts of deionized water, 4.2 parts of lauryl sulfuric acid sodium (Emal0; Kao Sekken), and 14 parts of polyoxy ethylene nonyl

phenyl ether (Emargen 935; Kao Sekken) were put in a 1-liter Erlenmeyer flask equipped with a stirrer, cooling device, temperature control device, and nitrogen guiding tube and heated to 80°C under stirring. Also, separately, 20 parts of potassium persulfuric acid dissolved in 60 parts of deionized water were put in a 1-liter Erlenmeyer flask. After about 10 minutes, a mixture of 52.5 parts of 3-(a) additive reaction substance, 56 parts of styrene, 128 parts of methacrylic acid ethyl, 109 parts of acrylic acid n-butyl, and 4.5 parts of acrylic acid was dripped into the flask for 3 hours. The reaction was conducted at 80°C under the nitrogen gas flow. The remaining persulfuric acid potassium was dripped into the flask for 3 hours and 30 minutes simultaneous to the dripping of the monomer mixture. After the completion of monomer mixture dripping, the liquid temperature was maintained at 80°C for 2 hours to complete the reaction. With this method, an emulsion (non-evaporative substance = 44.8%, viscosity = 400 cp, and average molecular count = 150,000) was obtained.

Reference example 3:

(A)

Soy bean oil fatty acid	235 parts
Methacrylic acid glycidyl	119
Hydroquinone	0.4
Tetra ethyl ammonium bromide	0.2

The abovementioned substances (A) were put in a reaction vessel and reacted under stirring at 140 - 150°C. The epoxy group and carboxy group addition reaction was traced while the remaining carboxyl group amount was measured. The reaction needed about 4.5 hours for completion.

(B)

100 parts of ethyl cellosolve were put in a reaction vessel and heated to 120°C. Next, a mixture of the following ratios of materials was dripped into this solution over the duration of 2 hours. The reaction was performed under the nitrogen gas flow.

(A) addition reaction product	60 parts
Methacrylic acid n-butyl	12
Styrene	15
Acrylic acid	13
Azobis isobutyronitrile	4

1 hour after the dripping, 1 part of azobis isobutyronitrile was added to the reaction solution, and the solution was maintained at 120°C for 2 hours to complete the reaction. Then, the solvent was /440 removed at 120°C under a reduced pressure. As a result, a soy bean oil fatty acid modified acryl polymer (non-evaporative substance = 96%; acid value = 95) was obtained.

(C)

78 parts of soy bean oil fatty acid modified acryl polymer obtained in (B), 10 parts of butyl cellosolve, 400 parts of deionized

water, and 12 parts of dimethyl ethanol amine were put in a 1-liter Erlenmeyer flask equipped with a stirrer, cooling device, and temperature control device, and the tall oil fatty acid modified acryl polymer was thoroughly dissolved in water, and heated to 120°C. Next, 5 parts of azobis cyano valeic acid were dissolved in 55 parts of deionized water and 4.7 parts of dimethyl ethanol amine. Then, 80% of this material was put in the reaction vessel and a mixture consisting of 25 parts of 4-(a) addition substance, 107.5 parts of methacrylic acid methyl, 35 parts of styrene, and 82.5 parts of acrylic acid n-butyl was dripped into the flask for 2 hours. After the completion of dripping, the remaining azobis cyano valeic acid aqueous solution was put in and maintained at 80 °C for 2 hours to complete the reaction. The non-evaporative substance of the emulsion was 40.2%, and the viscosity was 1100cp.

Reference example 4:

(A)

Linseed oil fatty acid	237 parts
Methacrylic acid glycidyl	119
Hydroquinone	0.4
Tetra ethyl ammonium bromide	0.2

The abovementioned substances (A) were put in a reaction vessel and reacted under stirring at 170 - 180°C. The epoxy group and carboxy group addition reaction was traced while the remaining

carboxyl group amount was measured. The reaction needed about 3 hours for completion.

(B)

300 parts of ethyl cellosolve were put in a 3-liter Erlenmeyer flask equipped with a stirrer, cooling device, and temperature control device and heated to 120°C. Next, a mixture of the following ratios of materials was dripped into this solution over the duration of 3 hours. The reaction was performed under the nitrogen gas flow.

(A) addition reaction product	300 parts
Methacrylic acid n-butyl	200
Azobis isobutyronitrile	15

1 hour after the dripping, 5 parts of t-butyl peroxy 2-ethyl hexanate were added to the reaction solution, and the solution was maintained at 120°C, to which 310 parts of anhydrous maleic acid were added and reacted at 220 - 230°C for about 4 hours. After the reaction, the solvent and non-reacted anhydrous maleic acid were removed with the reduced pressure distillation. Then, the open-ring reaction was provided with water, to which 180 parts of cellosolve were added. Furthermore, this material was neutralized with 1.0 equivalent triethyl amine at 80°C under stirring. Then, deionized water was added. As a result, partly maleic-processed aqueous solution of fatty acid modified acryl copolymer (non-evaporative substance = 33%) was obtained.

Reference example 5:

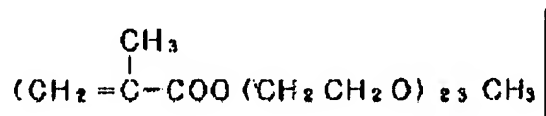
(A)

Linseed oil fatty acid	237 parts
Methacrylic acid glycidyl	119
Hydroquinone	0.4
Tetra ethyl ammonium bromide	0.2

The abovementioned substances (A) were put in a reaction vessel and reacted under stirring at 170 - 180°C. The epoxy group and carboxy group addition reaction was traced while the remaining carboxyl group amount was measured. The reaction needed about 3 hours for completion.

(B)

400 parts of deionized water, 12 parts of addition substances (A), 3 parts of polyethylene glycol monomethacrylate (Blenmer PE-350; product of Nihon Yushi) expressed as below:



9.6 parts of styrene, 18 parts of methacrylic acid methyl, 15 parts of acrylic acid n-butyl, 2.4 parts of acrylic acid, 0.3 part of persulfuric acid potassium, and 1.5 parts of sulfurous acid hydrogen sodium were put in a 1-liter Erlenmeyer flask equipped with a stirrer, cooling device, temperature control device, and nitrogen guiding tube and heated to 60°C under the nitrogen gas flow. Once heated, a solution consisting of 1.2 parts of persulfuric acid

potassium dissolved in 50 parts of deionized water and a separately prepared solution consisting of 48 parts of adding substances (A), 12 parts of polyethylene glycol monomethacrylate, 38.4 parts of styrene, 72 parts of methacrylic acid methyl, 60 parts of acrylic acid n- /441 butyl, and 9.6 parts of acrylic acid were individually dripped for the duration of 2 hours and 30 minutes. The reaction temperature was maintained at 60°C. After the completion of liquid dripping, the solution was maintained at 60°C for 2 hours to complete the reaction. As a result, an emulsion having 39.4% of non-evaporative substance and viscosity of 200 cp was obtained. The average molecular count of this resin was about 200,000.

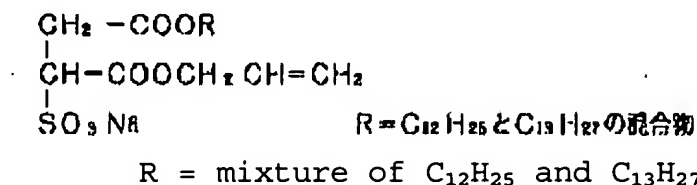
Reference example 6:

(A)

Safflower oil fatty acid	236 parts
Methacrylic acid glycidyl	131
Hydroquinone	0.4
Tetra ethyl ammonium bromide	0.2
Ethyl cellosolve	89

The abovementioned substances (A) were put in a reaction vessel and reacted under stirring at 130 - 140°C. The epoxy group and carboxy group addition reaction was traced while the remaining carboxyl group amount was measured. The reaction needed about 4 hours for completion. While this material was maintained at 120°C, the solvent was removed at a reduced pressure under stirring.

400 parts of deionized water, 3 parts of addition substances (A), 18.8 parts (valid substance = 7.5 parts) of Eleminol JS-2 (Sanyo Kasei Kogyo) expressed as below:



15 parts of styrene, 18 parts of methacrylic acid methyl, 16.8 parts of acrylic acid 2-ethyl hexyl, 1.2 parts of acrylic acid, 16.8 part of acrylic acid 2-ethyl hexyl, 1.2 parts of acrylic acid, and 0.6 parts of persulfuric acid ammonium were put in a 1-liter Erlenmeyer flask equipped with a stirrer, cooling device, temperature control device, and nitrogen guiding tube and heated to 80°C under the nitrogen gas flow. Once heated, a solution consisting of 0.9 parts of persulfuric acid ammonium dissolved in 50 parts of deionized water and a separately prepared solution consisting of 12 parts of adding substances (A), 60 parts of styrene, 72 parts of methacrylic acid methyl, 67.2 parts of acrylic acid 2-ethyl hexyl, and 4.8 parts of acrylic acid were dripped for 3 hours. The reaction temperature was maintained at 80°C. After the completion of liquid dripping, the solution was maintained at 80°C for 2 hours to complete the reaction. As a result, an emulsion having 37.4% of non-evaporative substance and viscosity of 120 cp was obtained. The average molecular count of this resin was about 150,000.

Reference example 7:

(A)

Linseed oil fatty acid	237 parts
Methacrylic acid glycidyl ethyl	130
Hydroquinone	0.4

The abovementioned substances (A) were put in a reaction vessel and reacted under stirring at 110 - 120°C. The aziridinyl group and carboxy group addition reaction was traced while the remaining carboxyl group amount was measured. The reaction needed about 3 hours for completion.

(B)

370 parts of deionized water, 4.2 parts of lauryl sulfuric acid sodium (Emal0, Kao Sekken), and 14 parts of polyoxy ethylene nonyl phenyl ether (Emalgen 935, Kao Sekken) were put in a 1-liter Erlenmeyer flask equipped with a stirrer, cooling device, temperature control device, and nitrogen guiding tube and heated to 80°C under stirring. Then, 20 parts of a separately prepared solution consisting of 1.4 parts of persulfuric acid potassium dissolved in 60 parts of deionized water were put in a 1-liter Erlenmeyer flask. About 10 minutes later, a mixture consisting of 52.5 parts of adding substances (A), 56 parts of styrene, 128 parts of methacrylic acid methyl, 109 parts of acrylic acid n-butyl, and 4.5 parts of acrylic acid was dripped over the duration of 3 hours. The reaction temperature was maintained at 80°C under a nitrogen gas flow. Then, simultaneously to the abovementioned monomer mixture dripping, the

remaining persulfuric acid potassium was dripped at a speed for allowing the completion of dripping within 3 hours and 30 minutes. After the completion of monomer mixture, the solution was maintained at 80°C for 2 hours to complete the reaction. As a result, an emulsion having 43.5% of non-evaporative substance and viscosity of 350 cp was obtained. The average molecular count of this resin was about 150,000.

Reference example 8:

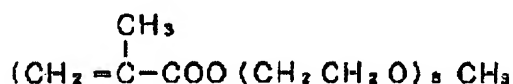
(A)

Tall oil fatty acid	235 parts	
Methacrylic acid glycidyl methyl	119	
Hydroquinone	0.4	
Tetra ethyl ammonium bromide	0.2	<u>/442</u>

The abovementioned substances (A) were put in a reaction vessel and reacted under stirring at 80 - 90°C. The aziridinyl group and carboxy group addition reaction was traced while the remaining carboxyl group amount was measured. The reaction needed about 4.5 hours for completion.

(B)

350 parts of deionized water, 22.5 parts of addition substances (A), 15 parts of methoxy polyethylene glycol mono methacrylate (NK ester M-9G, Shin Nakamura Kagakusha) expressed as below:



27 parts of methacrylic acid methyl, 5.3 parts of acrylic acid n-butyl, and 9 parts of acrylic acid n-butyl were put in a 1-liter Erlenmeyer flask equipped with a stirrer, cooling device, temperature control device, and nitrogen guiding tube and stirred under the nitrogen gas flow. Then, 6 parts of azobis cyano valeic acid were dissolved in 100 parts of deionized water containing 5.7 parts of amine. Then, 80% of this aqueous solution was put in an Erlenmeyer flask and heated to 80°C. Once heated to 80°C, a mixture consisting of 67.5 parts of addition reaction substances (A), 30 parts of methoxy polyethylene glycol, 81 parts of methacrylic acid methyl, 15.7 parts of methacrylic acid n-butyl, and 27 parts of acrylic acid n-butyl was dripped for 1 hour and 30 minutes. After the completion of liquid dripping, the remaining azobis cyano valeic acid aqueous solution was put in and maintained at 80°C for 2 hours to complete the reaction. As a result, an emulsion having 39.2% of non-evaporative substance and viscosity of 200 cp was obtained. The average molecular count of this resin was about 60,000.

Reference example 9:

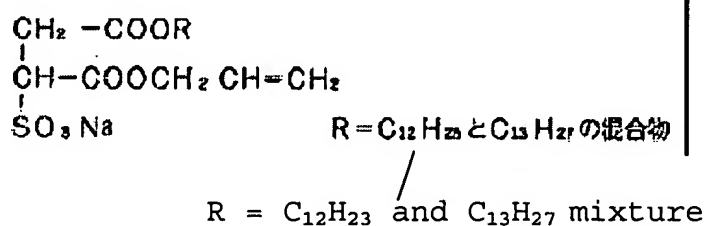
(A)

Soy bean oil fatty acid	142 parts
Dehydrated castor oil fatty acid	95
Methacrylic acid glycidyl ethyl	130
Hydroquinone	0.3

The abovementioned substances (A) were put in a reaction vessel and reacted under stirring at 130 - 140°C. The aziridinyl group and carboxy group addition reaction was traced while the remaining carboxyl group amount was measured. The reaction needed about 1 hour for completion.

(B)

400 parts of deionized water, 12 parts of addition reaction substances (A), 22.5 parts (valid substance = 9 parts) of Eleminol JS-2 (Sanyo Kasei Kogyosha) expressed as below:



9.6 parts of styrene, 18 parts of methacrylic acid methyl 15 parts of acrylic acid n-butyl, 2.4 parts of acrylic acid, 0.3 parts of persulfuric acid potassium, and 1.5 parts of sulfurous acid were put in a 1-liter Erlenmeyer flask equipped with a stirrer, cooling device, temperature control device, and nitrogen guiding tube and heated to 60°C. Once heated, a solution prepared by dissolving 1.2 parts of persulfuric acid potassium in 50 parts of deionized water and a separately prepared solution consisting of 48 parts of addition reaction substances (A), 38.4 parts of styrene, 72 parts of methacrylic acid methyl, 60 parts acrylic acid n-butyl, and 9.6 parts of acrylic acid were individually dripped for 2 hours and 30 minutes.

The reaction temperature was maintained at 60°C. After the completion of liquid dripping, the substance was maintained at 60°C for 2 hours to complete the reaction. As a result, an emulsion having 38.7% of non-evaporative substance and viscosity of 100 cp was obtained. The average molecular count of this resin was about 200,000.

Operational examples 5 - 16:

By performing the same method as described in the operational example 1, except that the compositions were changed to the materials shown in Table 1, aqueous paint compositions 5 - 16 were obtained. Also, for comparison purpose, the following aqueous paint composition was prepared.

Comparison example 1:

(A)

Titanium oxide (Taibake 820, Ishihara Sangyo)	20 parts
Calcium carbonate (Super 3S, Maruo Calcium)	15
Pigment dispersant (SMA 1440H, Daiichi Kogyo Yakuhin)	5
Water	10

(B)

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Fatty acid modifiable oxidative polymerizing aqueous emulsion described in the reference example 1

(resin solid substance amount)	25 parts
Ethylene glycol	5

Water	19.5
Naphtene acid cobalt (Dicknate 3111, by Dainihon Ink Kagaku)	0.5

The materials (A) were well stirred and granulated into particles having the granular diameter of 50 μ or less using a SG mill. Then, the materials (B) were added under stirring to obtain the paint composition of comparison example 1.

Comparison example 2:

(A)

Iron oxide (Todacolor KNO, Toda Kogyo)	5 parts
Cyanamide lead (rust-proofing pigment)	15
Calcium carbonate (Super 3S, Maruo Calcium)	15
Pigment dispersant (SMA 1440H, Daiichi Kogyo Yakuhin)	5
Water	10

(B)

Styrene acryl aqueous emulsion resin (Boncoat EC740, Dainihon Ink Kagaku)	45 parts
Ethylene glycol	5

The materials (A) were well stirred and granulated into particles having the granular diameter of 50 μ or less using a SG mill. Then, the materials (B) were added under stirring to obtain the paint composition of comparison example 2.

Comparison example 3:

(A)

Iron oxide (Todacolor KNO, Toda Kogyo)	5 parts
Cyanamide lead (Rust-proofing pigment)	15
Calcium carbonate (Super 3S, Maruo Calcium)	15
Tall oil phthalic acid resin mineral spirit (solvent)	15
Mineral spirit (solvent)	10

Oil length = 60% Soy bean oil modifiable

Non-evaporative component = 70%

Acid value = 5

Solvent = mineral spirit

(B)

Tall oil phthalic acid resin	21
25% naphthene acid lead (drying agent)	1.0
5% naphthene acid cobalt (drying agent)	0.5
Mineral spirit (solvent)	17.5

The materials (A) were well stirred and granulated into particles having the granular diameter of 50 μ or less using a SG mill. Then, the materials (B) were added under stirring to obtain the paint composition of comparison example 3.

The aqueous paint compositions of operational examples 1 - 16 and comparison examples 1 - 3 were left untouched in a fixed-temperature room (60°C) for 2 weeks. Then, the condition of each paint was examined. Also, each paint was brush-coated on a polished

copper plate for 100 g/m². Then, 24 hours later, each paint was again brush-coated on a polished copper plate for 100 g/m². Then, after each plate was dried for 7 days in the 20°C atmosphere, each coat film property was examined. The results are shown in Table 1.

Operational example Table 1

		第 1									
		実施例	1	2	3	4	5	6	7	8	9
a)	トダカラー-KNO	5	5	5	5	5	5	5	5	5	5
b)	サビ止め顔料										
c)	スーパー3S	15	15	15	15	25	25	5	25	15	
d)	SMA1440H	5	5	(10)	(10)	5	5	5	5	5	5
e)	水	10	10	10	10	10	10	10	10	10	10
f)	脂肪酸変性酸化重合型 水性エマルジョン樹脂	25	25	20	20	25	25	25	25	25	25
		参考例	参考例	参考例	参考例	参考例	参考例	参考例	参考例	参考例	参考例
g)	エチレングリコール	1	2	1	3	2	3	1	5	6	
h)	水	5	5	5	5	5	5	5	5	5	5
i)	5%ナフチン酸コバルト	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5
j)	シアナミド鉛	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
k)	リン酸亜鉛	15		15	15	5					
l)	止メタボウ酸		15				5	25			
m)	めバリウム									5	15
n)	鉛酸カルシウム										
o)	料モリブデン酸亜鉛										
p)	(注1) 塗料安定性	○	◎	○	○	◎	◎	◎	◎	◎	◎
q)	(注2) 耐水性	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎
r)	(注3) 耐アルカリ性	◎	○	○	○	○	○	○	○	○	○
s)	(注4) 耐ソルト	◎	○	○	◎	○	○	○	○	○	○
t)	(注5) 剥離強度	12kg	13kg	13kg	12kg	15kg	13kg	12kg	14kg	14kg	
u)											

Key A...Reference example; B...Comparison example; C...Refer to another sheet; a...Toda Color KNO; b...Rust-proofing pigment; c...Super 3S; d...SMA1440H; e...Water; f...Fatty acid modifiable oxidative polymer type aqueous emulsion resin; g...Ethylene glycol; h...Water; i...5% naphthene acid cobalt; j...Rust-proofing pigment; k...Cyanamide lead; l...Phosphoric acid zinc; m...Metha boric acid barium; n...Lead acid calcium; o...Molybdenum acid zinc; p...Capacity comparison; q...Note 1) Paint stability; r...Note 2) Water resistance; s...Note 3) Alkali resistance; t...Note 4) Anti salt spray characteristic; u...Note 5) Peeling strength

Table 1 (continued)

	10	11	12	13	14	15	16	比較例 1	比較例 2	比較例 3	
a)	5	5	5	5	5	5	5	別	別	別	B
b)	5	5	5	5	5	5	5				
c)	25	15	5	15	5	5	5				
d)	5	5	5	5	5	5	5				
e)	10	10	10	10	10	10	10				
f)	25	25	25	25	25	25	25	試	試	試	A
	参考例	参考例	参考例	参考例	参考例	参考例	参考例				
g)	7	8	9	1	5	7	9				
h)	5	5	5	5	5	5	5				
i)	19.5	19.5	19.5	19.5	19.5	19.5	19.5				
j)	0.5	0.5	0.5	0.5	0.5	0.5	0.5				
k)					25						
l)											
m)	5	15				25					
n)			5	15			25				
o)	□	□	□	□	□	□	□	□	△	○	
p)	□	□	□	□	□	□	□	□	△	△	
q)	○	○	○	○	○	○	○	○	○	×	
r)	○	○	○	○	○	○	○	○	○	○	
s)	○	○	○	○	○	○	○	△	×	○	
t)											
u)	15kg	13kg	13kg	12kg	12kg	13kg	15kg	18kg	16kg	6kg	

Note 1) Paint state after left untouched for 2 weeks in a 60°C temperature-fixed room.

□: No abnormality; ○: Slightly viscous; □: Extremely viscous; X: Hard cake

Note 2) Coated film abnormality observed after the film was soaked in 20°C water for 48 hours.

□: No abnormality; ○: Partially slightly swollen; □: Small swollen parts over the entire surface; X: Many large swollen areas

Note 3) Coated film abnormality observed after the film was soaked in a 4% NaOH aqueous solution for 1 hour.

□: No abnormality; O: Slightly swollen; □: Tendency of dissolving; X: Dissolved

Note 4) Rust occurrence after spraying 5% salt water (40°C) for 240 hours.

□: No abnormality; O: Slightly swollen; □: Small swollen parts and rusted areas; X: Many rusted areas and film peeling

Note 5) Adhesion tester (Elcometer Co.) was used.